Supporting Information

Multiple Olefin Metathesis Polymerization that Combines All Three Olefin Metathesis Transformations: Ring-Opening, Ring-Closing, and Cross Metathesis

Ho-Keun Lee,[†] Ki-Taek Bang,[†] Andreas Hess,[†]

Robert H. Grubbs[‡] and Tae-Lim Choi[*†]

[†]Department of Chemistry, Seoul National University, Gwanak-ro, Gwanak-gu, Seoul, Korea

[‡]Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125, United States

Email : tlc@snu.ac.kr

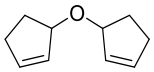
Table of Contents

General experimental

All reagents which are commercially available were used without further purification. For polymerization, THF was distilled from sodium and benzophenone. THF was degassed by Ar bubbling for 10 minutes before using on polymerization. Thin-layer chromatography (TLC) was carried out on MERCK TLC silica gel 60 F254 and flash column chromatography was performed using MERCK silica gel 60 (0.040~0.063 mm). 1H-NMR was recorded by Varian/Oxford As-500 (500 MHz) spectrometers. THF SEC (size exclusion chromatography) was carried out at 1.0 mL/min. SEC for polymer analysis was carried out with Waters system (1515 pump, 2414 refractive index detector) and Shodex GPC LF-804 column on samples diluted in 0.001-0.003 wt % by THF (HPLC grade, Honeywell Burdick & Jackson®) and filtered with a 0.2-μm PTFE filter. The columns were thermostatted at 35 ℃.

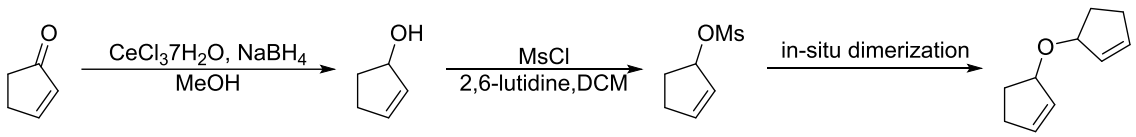
Monomer and polymer preparation

Preparation of monomer 1



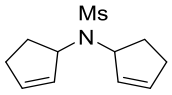
Ether formation from allylic alcohols catalyzed by samarium trichloride By Ouertani, Mohsen; Collin, Jacqueline; Kagan, Henri B. From *Tetrahedron* **1985**, 41(18), 3689-93.

^{1}H-NMR and ^{13}C-NMR analysis data are available in the same literature.



To solution of 2-cyclopentenone(2.49 g, 30 mmol) and cerium trichloride heptahydrate(12.30 g, 33 mmol) in MeOH(60 ml), $NaBH_4$(2.0 g,36 mmol) was added slowly with ice bath and stirred for 15 min. Reaction mixture was extracted with diethyl ether and water and dried with $MgSO_4$. Cyclopentenol is purified by silica gel column chromatography (Ethyl Acetate /Hexane = 1/1) to yield corresponding alcohol with 60-80 % yield. With cyclopentenol(0.87 g, 10 mmol) and DCM(25 ml) solution, 2,6-lutidine(1.3 ml, 12 mmol) was added to solution. After 5 mins, Mesyl chloride (0.41 ml, 5 mmol) is added slowly. During the reaction, not only Mesylate but also Monomer1 was synthesized by in-situ dimerization. Yield of Corresponding ether is 40 %.

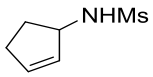
Preparation of monomer 2



^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.0 (2H, m), 5.68(H, m), 5.62 (1H, m), 4.68 (1H, m), 2.88 (1H, s), 2.55 (2H, m), 2.29 (4H, m), 1.96 (2H, m)

^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 135.55, 135.13, 130.29, 129.58, 63.31, 63.28, 42.47, 42.11, 31.49, 31.45, 29.89, 29.49

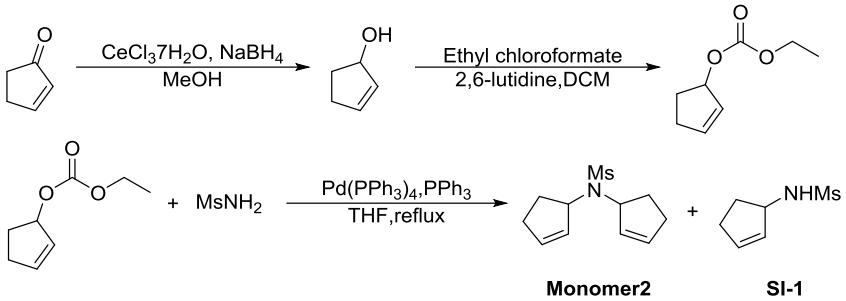
HRMS (ESI) calcd.for $(C_{11}H_{17}NO_2S)^-$ Na^+ 250.0872 found, 250.0871



^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.96 (1H, m), 5.71 (1H, m), 4.53 (1H, m), 4.39 (1H, m), 2.97 (1H, s), 2.28-2.42 (3H, m), 1.71 (1H, m)

^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 136.24, 130.56, 59.89, 41.60, 32.09, 30.92

HRMS (ESI) calcd.for $(C_6H_{11}NO_2S)^-$ Na^+ 184.0403 found, 184.0402

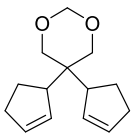


To solution of 2-cyclopentenone (2.49 g, 30 mmol) and cerium trichloride heptahydrate (12.30 g,33 mmol) in MeOH (60 ml), $NaBH_4$ (2.0 g,36 mmol) was added slowly with ice bath and stirred for 15 min. Reaction mixture was extracted with diethyl ether and water and dried with $MgSO_4$. Cyclopentenol is purified by silica gel column chromatography (ethyl acetate /hexane = 1/1) to yield corresponding alcohol with 60-80 % yield

With cyclopentenol (3 g, 35.7 mmol) and DCM solution, 2,6-lutidine(1.2 equiv) was added to solution. After 5mins, Ethyl chloroformate(1.1 equiv) is added slowly. Corresponding carboxylate is purified by silica gel column chromatography (ethyl acetate / hexane = 1/10) with 70 % yield

p-Mesylsulfonamide (570 mg, 5.5 mmol) was added to THF under argon at room temperature. The mixture was stirred for 10 min. To this was added $Pd(PPh)_4$ (0.65 g,0.55 mmol) and PPh_3 (290 mg,1,1 mmol), followed by cyclopent-2-enyl carboxylate(2.2 g,14 mmol). The resulting bright yellow solution was heated under reflux for 10 h. The mixture was then partitioned between diethyl ether and water. The organic layer was separated, and the aqueous extracted with diethyl ether. The organic extracts were combined, dried over $MgSO_4$ filtered, and concentrated in vacuo. Purification of the resulting brown residue on silica gel (1:10 ethly acetate/ hexanes) gave M2 (50 % yield).

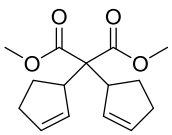
Preparation of monomer 3



^{1}H NMR (500MHz, $CDCl_3$, ppm) δ 5.8 (4H, m), 3.75 (4H, t), 3.04 (2H, m), 2.28 (4H, m), 1.91 (2H, s), 1.78 (2H, m)

^{13}C NMR (400MHz, $CDCl_3$, ppm) δ 132.02, 131.73, 131.31, 131.14, 94.09, 93.93, 72.21, 71.55, 70.93, 48.40, 48.36, 32.00, 31.86, 25.14, 24.93

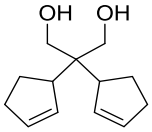
HRMS (CI+) calcd.for $C_{14}H_{21}O_2^+$ 222.1541 found, 222.1537



^{1}H NMR (500MHz, $CDCl_3$, ppm) δ 5.72 (4H, m), 3.62 (6H, m), 3.43 (2H, broad), 2.21 (4H, broad), 2.00 (2H, m), 1.77(1H, m), 1.65 (1H, m)

^{13}C NMR (400MHz, $CDCl_3$, ppm) δ 171.12, 170.86, 170.69, 132.12, 131.74, 131.28, 131.07, 65.16, 64.83, 51.86, 51.60, 51.48, 49.58, 49.52, 31.65, 31.51, 25.66, 25.35

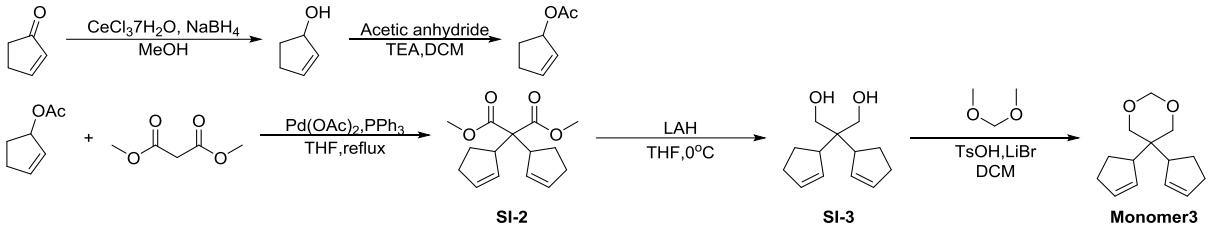
HRMS (ESI) calcd.for $(C_{15}H_{20}O_4)^-$ Na^+ 287.1254 found, 287.1254



^{1}H NMR (500MHz, $CDCl_3$, ppm) δ 5.90 (2H, m), 5.81 (2H, m), 3.78 (2H, m), 3.68 (2H, m), 2.99 (2H, m), 2.35 (6H, m), 1.92(2H, m), 1.80 (2H, m)

^{13}C NMR (400MHz, $CDCl_3$, ppm) δ 132.56, 132.43, 131.86, 131.72, 66.64, 66.44, 66.23, 48.30, 48.28, 46.30, 46.08, 32.09, 31.91, 24.70, 24.67

HRMS (CI+) calcd.for $C_{13}H_{21}O_2^+$ 209.1542 found, 209.1541



To solution of 2-cyclopentenone and cerium trichloride heptahydrate in MeOH, $NaBH_4$ was added slowly with ice bath and stirred for 15 min. Reaction mixture was extracted with diethyl ether and water and dried with $MgSO_4$. Cyclopentenol is purified by silica gel column chromatography (ethyl acetate /hexane = 1/1) to yield corresponding alcohol with 60-80 % yield

With cyclopentenol (3.0 g, 35 mmol) and DCM solution, TEA (4.55 ml, 45 mmol) & DMAP (0.43 g, 3.57 mmol) was added to solution. After 5mins, acetic anhydride (3.9 ml, 40 mmol) is added slowly. Corresponding acetate derivative is purified by silica gel column chromatography (ethyl acetate / hexane = 1/10) with 80 % yield

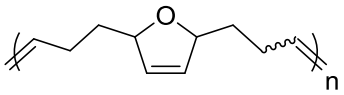
To a suspension of NaH (1.0 g, 42 mmol) in THF under argon at room temperature was added dimethylmalonate (1.9 ml, 12 mmol). The mixture was stirred for 10 min. To this was added $Pd(OAc)_2$ (0.27 g, 1.2 mmol) and PPh_3 (0.64 g, 2.5 mmol), followed by cyclopent-2-enyl acetate (3.23 g, 25 mmol). The resulting bright yellow-green solution was heated under reflux for 10 h. The mixture was then partitioned between diethyl ether and water. The organic layer was separated, and the aqueous extracted with diethyl ether. The organic extracts were combined, dried over $MgSO_4$ filtered, and concentrated in vacuum. Purification of the resulting brown residue on silica gel (1:10 Ethly acetate/ hexanes) gave dimethyl 2,2-di(cyclopent-2-en-1-yl)malonate (50 % yield).

dimethyl 2,2-di(cyclopent-2-en-1-yl)malonate(0.81 g, 3 mmol) was added to Ar-purged flask and dissolved in THF. Solution was cooled to 0℃ and lithium aluminum hydride (230 mg, 6 mmol) was added slowly. Reaction mixture was stirred for 2 hour until all ester groups were converted to alcohol. Resulting mixture was quenched by successive addition of water (1 ml per 1 g of LAH) in ice bath, 10 % NaOH solution (2 ml per 1 g of LAH), and water (3ml per 1g of LAH). Resulting mixture was filtered through celite pad and ecaporated under reduced pressure. Diol was purified by silica gel column chromatography (ethyl acetate / hexane = 1/3) to yield with over 90 %

2,2-di(cyclopent-2-en-1-yl)propane-1,3-diol(624mg,3mmol) was added to flask and dissolved in DCM(6 ml). Toluenesulfonyl acid (171 mg, 0.9 mmol) and Lithium bromid e(52 mg,0.6 mmol) is added to solution and methoxypropane (0.4 ml, 4.5 mmol) is added to solution. Reaction mixture was extracted with dichloromethane and water and dried with $MgSO_4$. M3 is purified by silica gel column chromatography (ethyl acetate / hexane = 1/5) to yield corresponding alcohol with 90 % yield

General procedure of Tandem RO/RCM polymerization

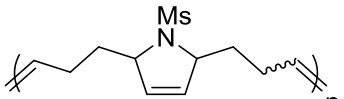
The monomer (0.1 mmol) was put into a 2 mL sized vial with septum and purged with Ar-gas. Degassed THF was added to the vial and stirred. A solution of metathesis catalyst in THF was prepared in another Ar-purged vial with septum, and solution was added using a microsyringe rapidly. Conversion was checked by TLC, and quantifed by crude ^{1}H-NMR after quenching by ethyl vinyl ether. The concentrated mixture was precipitated into methanol.



P1

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.78 (2H, m), 5.37 - 5.44 (2H, s), 4.82 (1H, s), 4.75 (1H, s), 2.06 (4H, broad), 1.58 (4H, s)

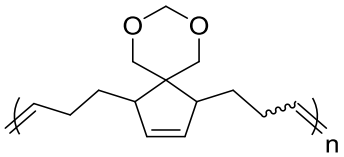
^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 131.46, 130.10, 130.05, 130.00, 129.96, 129.86, 129.79, 129.60, 129.54, 85.29, 85.18, 85.09, 36.72, 35.95, 35.87, 28.47, 28.21, 23.28, 22.97



P2

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.78 (2H, d), 5.41-5.45 (2H, m), 4.53 (1H, s), 4.32 (1H, s), 2.93 (1.5H, s), 2.73 (1.5H, s), 2.04-2.10 (4H, br), 1.59-1.95 (4H, m)

^{13}C NMR (400 MHz, $CDCl_3$, ppm)



P3

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 5.83 (1H, m), 5.73 (1H, m), 4.82 (2H, m), 3.87 (1H, s), 3.75 - 3.78(1H, d), 3.61 – 3.64 (1H, d), 3.47 (1H, s), 2.50 (1H, s), 2.33 (1H, s), 2.11 (2H, s), 1.98 (2H, s) , 1.66 (2H, s), 1.11 - 1.18 (2H, m)

^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 133.31, 133.16, 132.45, 132.04, 131.12, 130.24, 129.72, 94.01, 93.94, 71.54, 71.38, 69.72, 49.25, 48.94, 48.40, 45.60, 44.15, 32.23, 31.86,31.44, 31.04, 29.51, 26.11, 25.74, 24.93

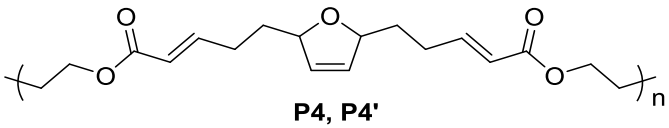
General procedure of multiple olefin metathesis polymerization

Sequential process by cross metathesis

To a flask charged with isolated polymer (0.32 mmol) and 1,4-butanediol diacrylate (62.5 mg, 0.32 mmol) in 1 ml of CH_2Cl_2, Grubbs Hoveyda second generation catalyst (3.5 mg). Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product was precipitated by hexane.

One pot process

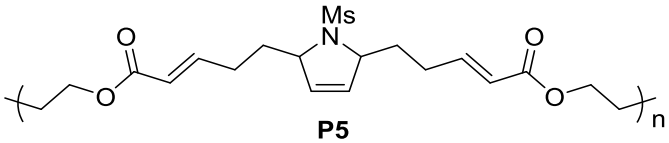
To a flask charged with dicyclopentene monomer (0.32 mmol) and 1,4-butanediol diacrylate (62.5 mg, 0.32 mmol) in 1 ml of CH_2Cl_2, Grubbs Hoveyda second generation catalyst (3.5 mg). Quick degassing by dynamic vacuum was conducted and the flask was fitted with a condenser and refluxed under argon for 6 hours. The product was precipitated by hexane.



P4, P4'

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 7.01 – 6.97 (2H, m), 5.79 - 5.87 (4H, m), 4.79 - 4.98 (2H, d), 4.16 (4H, s), 2.27 – 2.33 (4H, m), 1.75 (6H, s), 1.65-1.67 (2H, s)

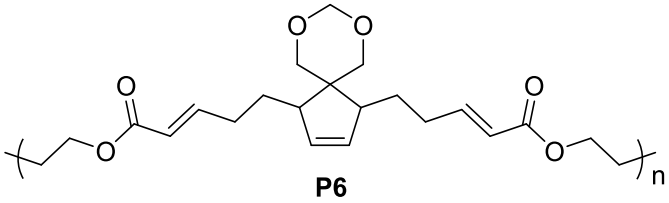
^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 166.40, 166.36, 148.93, 148.80, 130.59, 130.43, 130.05, 129.87, 121.28, 121.12, 84.88, 84.75, 63.59, 34.81, 33.97, 28.13, 27.72, 25.29



P5

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.91 – 7.00 (2H, m), 5.79 - 5.88 (4H, m), 4.63 (1H, s), 4.39 (1H, s), 4.16 (4H, s) 2.96 (1.5H, s), 2.74 (1.5H, s), 2.13-2.33 (2H, br), 1.89 (4H, m), 1.75 (4H, s)

^{13}C NMR (400 MHz, $CDCl_3$, ppm)

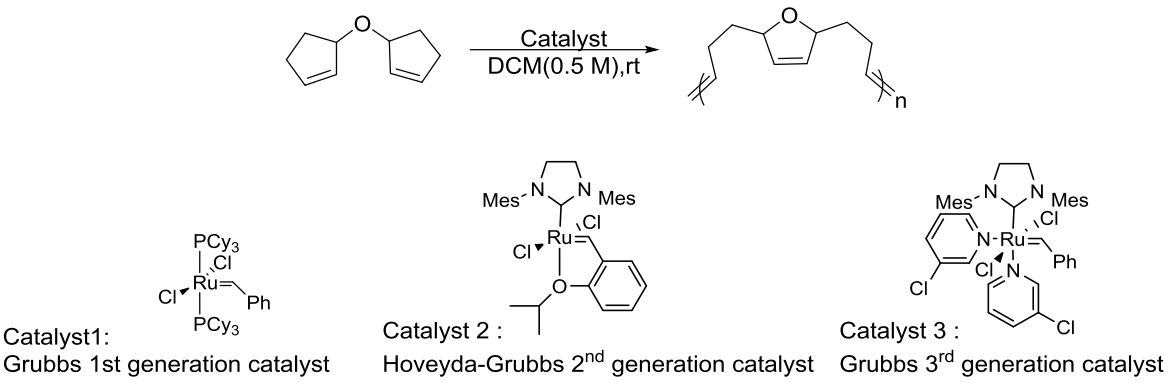


P6

^{1}H NMR (500 MHz, $CDCl_3$, ppm) δ 6.94 – 6.99 (2H, m), 5.74 - 5.87 (4H, m), 4.83 (2H, d), 4.16 (4H, s), 3.48 - 3.87 (4H), 2.20 - 2.53 (6H, broad), 1.76 (6H, s), 1.24-1.28 (2H, broad)

^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ 131.16, 132.45, 130.24, 94.01, 71.54, 71.38, 68.72, 49.25, 48.94, 48.40, 45.60, 44.15, 32.23, 31.86, 31.44, 31.04, 29.51

Catalyst reactivity comparison



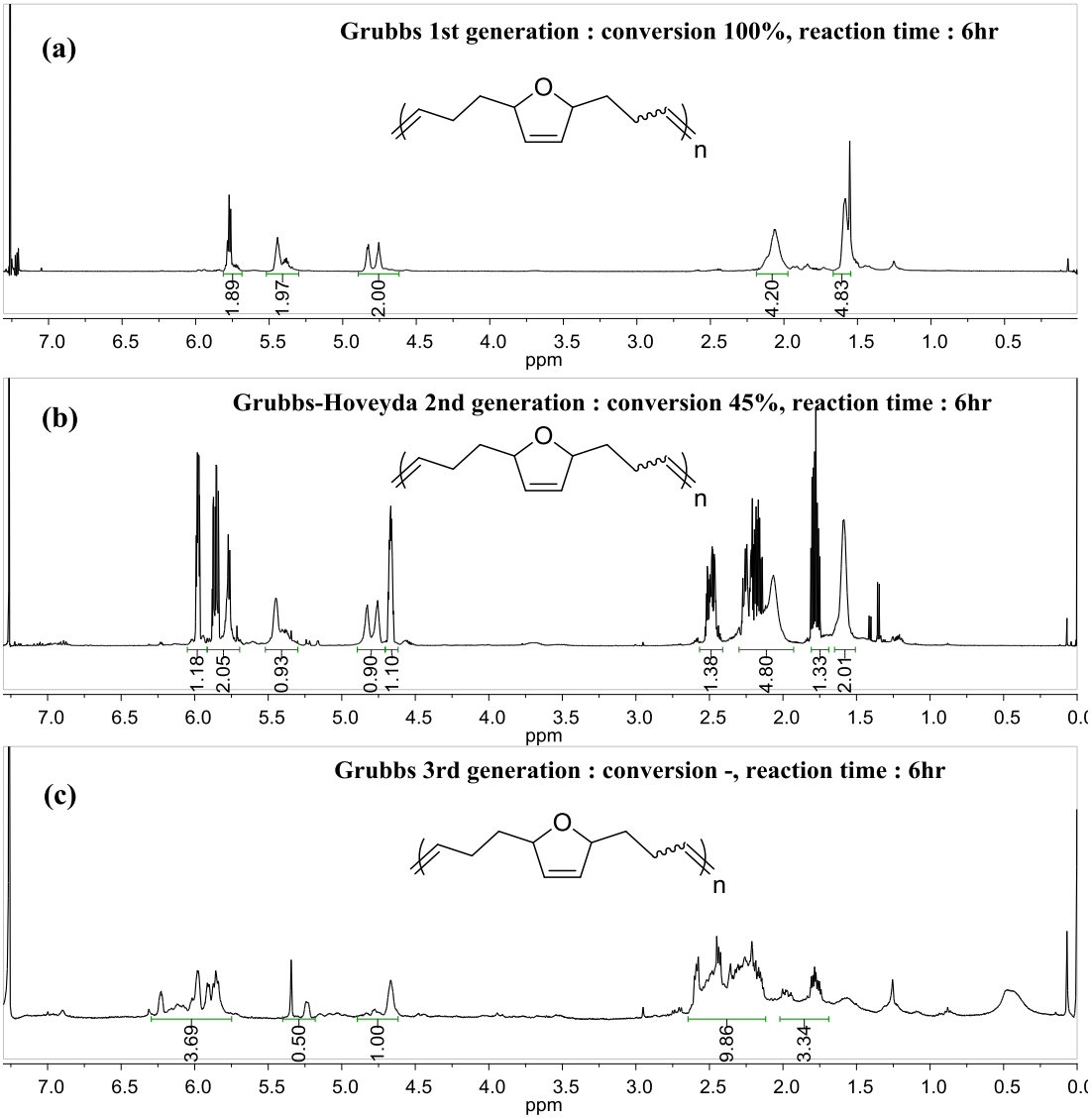


Figure S1. Catalyst reactivity comparison for Tandem RO/RCM polymerization (a) Grubbs 1st generation catalyst (b) Hoveyda-Grubbs 2nd generation catalyst (c) Grubbs 3rd generation catalyst

Polymer structure analysis by separation of diastereomeric repeat unit

In monomer structure, two stereogenic centers are exist. It caused complicated polymer structure by diastereomers. To get perfect structural analysis of polymers, ethenolysis reactions with monomer 1-3 were tried. Finally, corresponding repeat units were separated by column chromatography and analyzed for structure analysis of corresponding polymer.

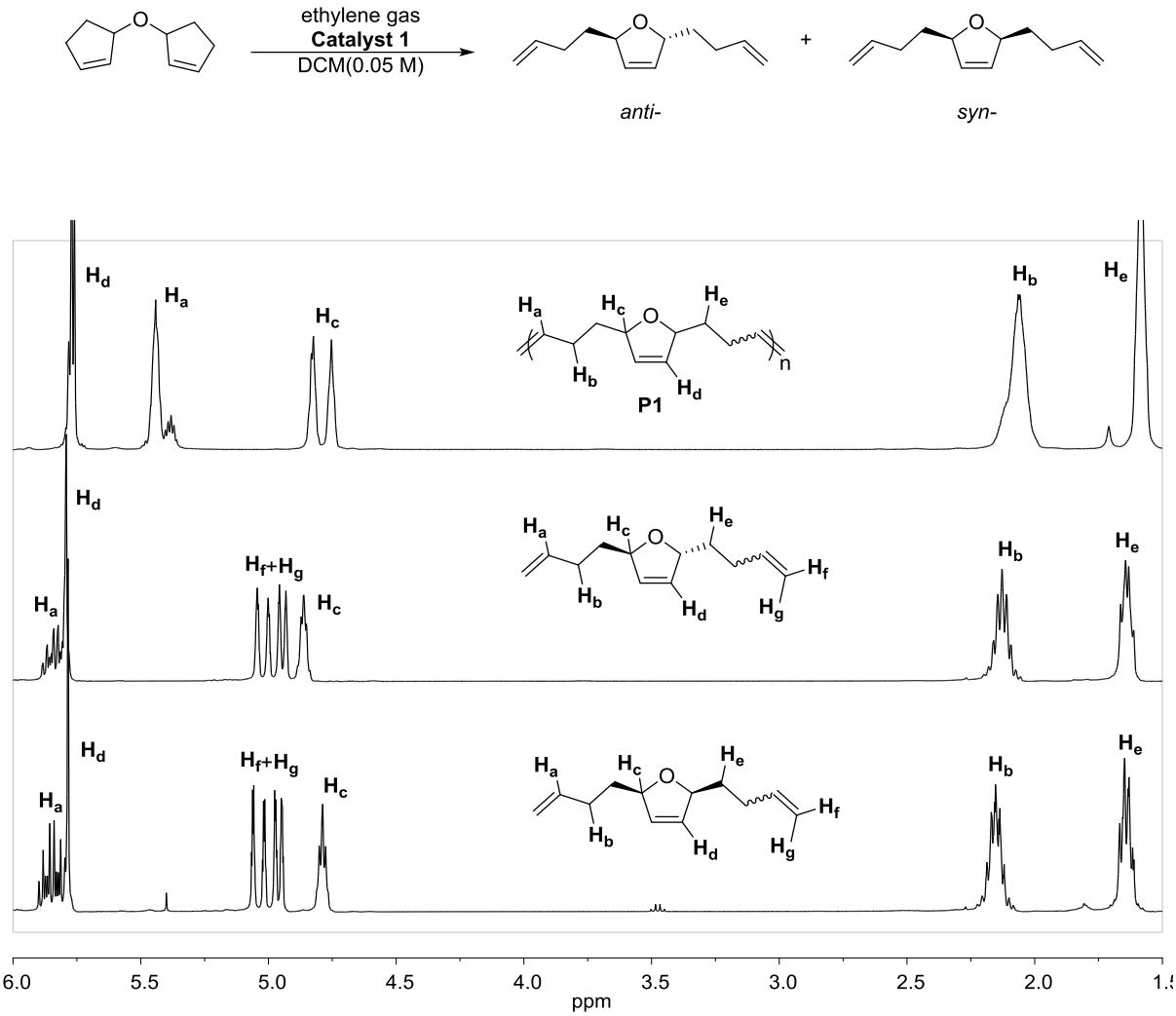


Figure S2. ^{1}H NMR of polymer and diastereomeric repeat units of P1

Without peaks from terminal olefin in diastereomeric repeat unit, each peaks in diastereomeric repeat units were well matched with polymeric peaks.

Molecular weight of *anti*- form: HRMS (CI+) calcd.for $C_{12}H_{19}O^{+}$ 179.1436 found, 179.1436

Molecular weight of *syn*- form: HRMS (CI+) calcd.for $C_{12}H_{19}O^{+}$ 179.1436 found, 179.1436

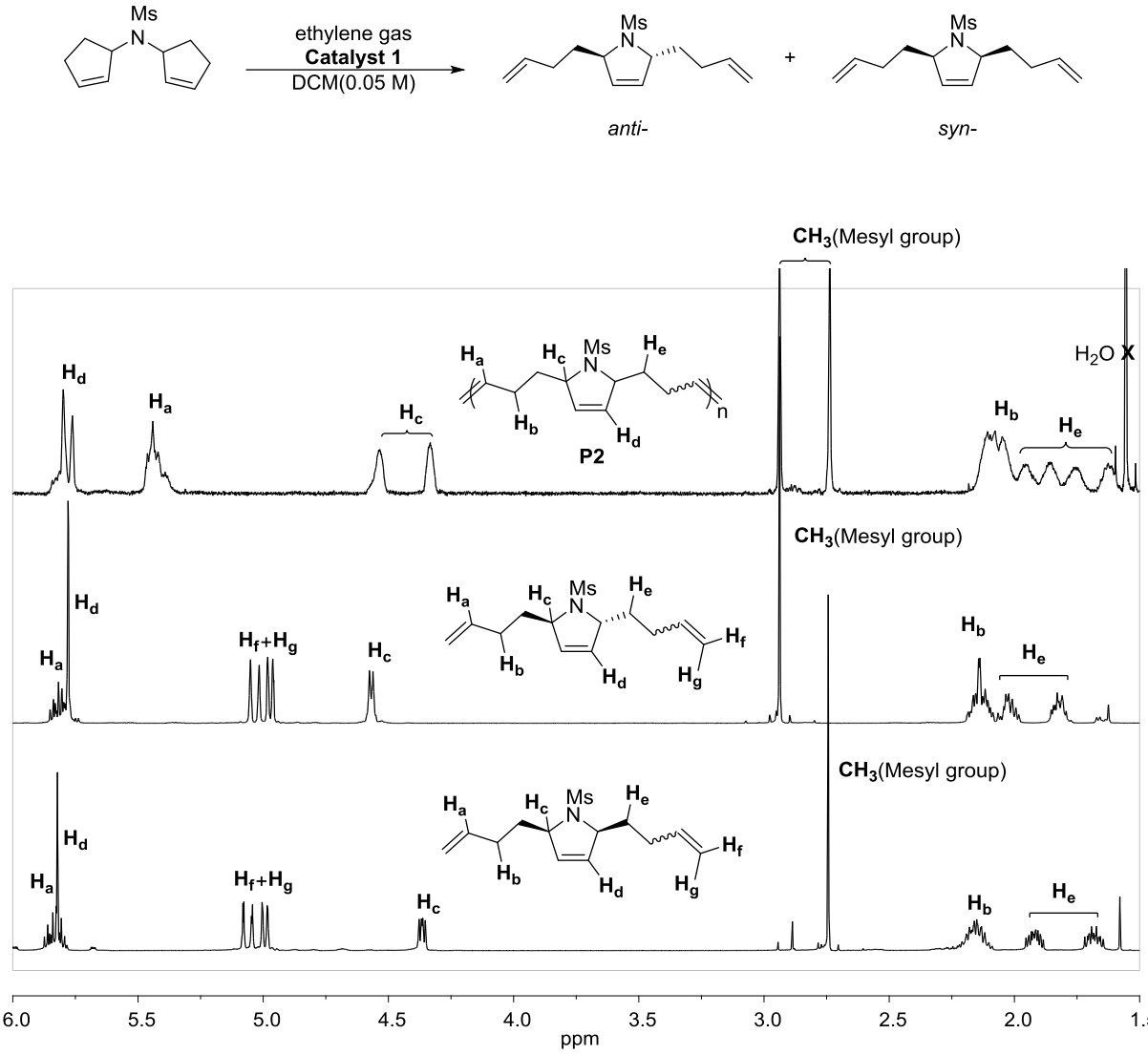
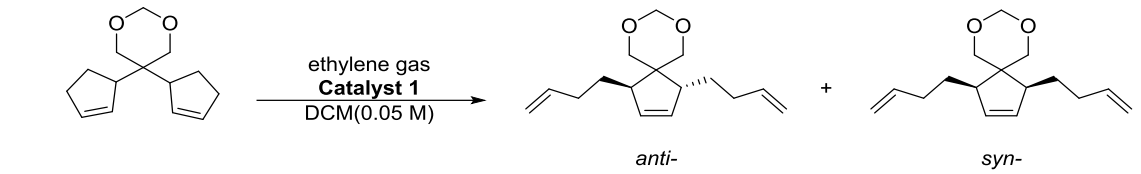


Figure S3. ^{1}H NMR of polymer and diastereomeric repeat units of P2

Without peaks from terminal olefin in diastereomeric repeat unit, each peaks in diastereomeric repeat units were well matched with polymeric peaks.

Molecular weight of *anti*- form: HRMS (CI+) calcd.for $C_{13}H_{22}NO_2S^+$ 256.1371 found, 256.1371

Molecular weight of *syn*- form: HRMS (CI+) calcd.for $C_{13}H_{22}NO_2S^+$ 256.1371 found, 256.1371



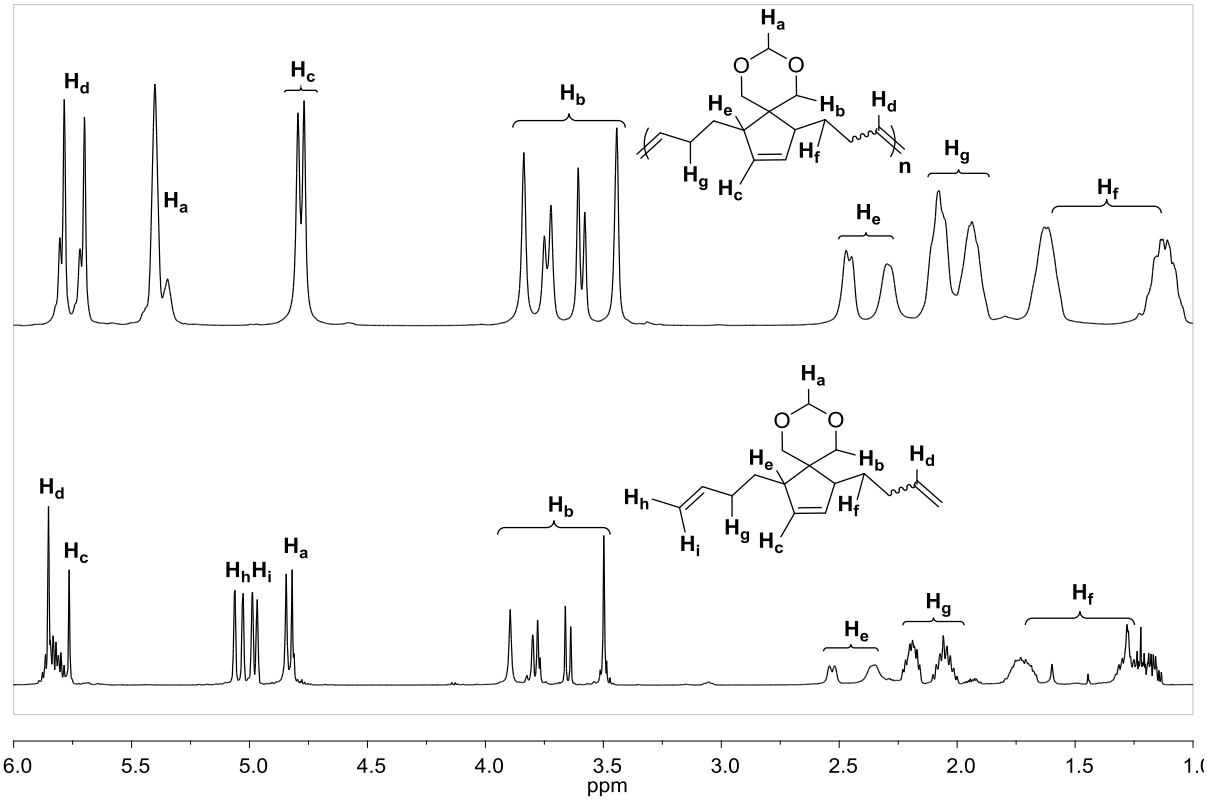


Figure S4. ^{1}H NMR of polymer and diastereomeric repeat unit of P3

In this case, diastereomeric repeat units were not able to separate by column chromatography. Only racemic repeat unit was separated by column chromatography. However the peaks of repeat unit were well analyzed and matched with corresponding polymer.

Molecular weight of *racemic* form: HRMS (CI+) calcd.for $C_{16}H_{25}O_2^+$ 249.1855 found, 249.1855

More detail spectrum and analysis of repeat units are attached at page 22 in this supporting data.

SEC trace of polymers

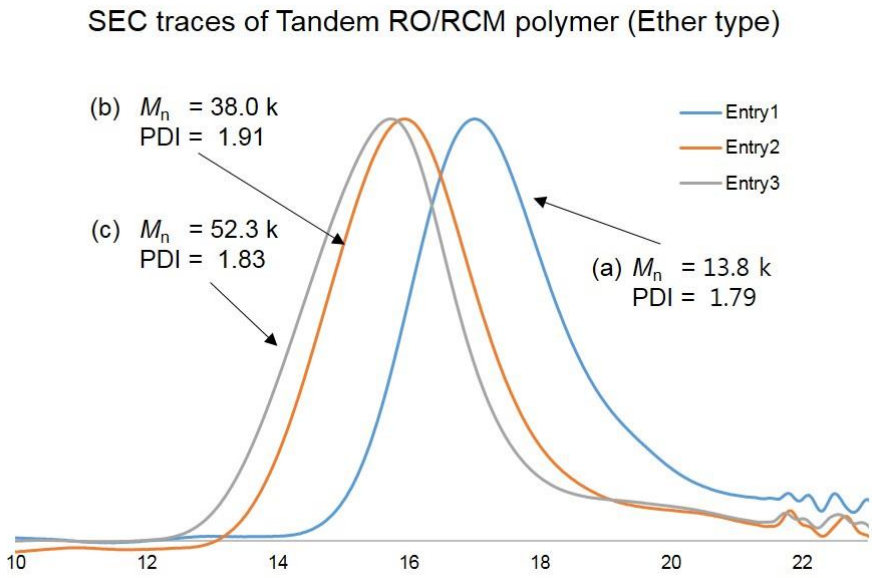


Figure S5. THF SEC trace for the tandem RO/RCM ether type polymer. Molecular weights and PDIs are listed in the figure. (a) SEC trace of Table1-Entry1. (b) SEC trace of Table1-Entry2. (c) SEC trace of Table1-Entry3.

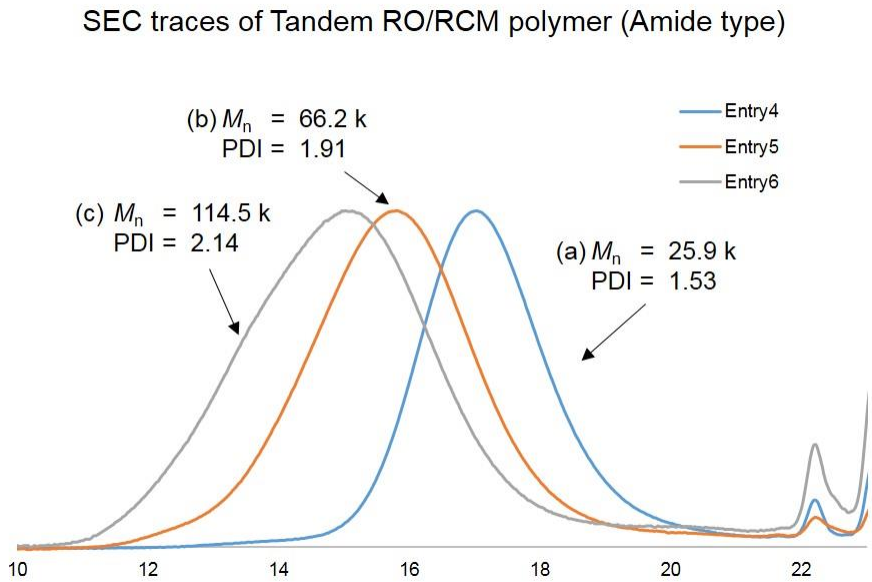


Figure S6. THF SEC trace for the tandem RO/RCM amide type polymer. Molecular weights and PDIs are listed in the figure. (a) SEC trace of Table1-Entry4. (b) SEC trace of Table1-Entry5. (c) SEC trace of Table1-Entry6.

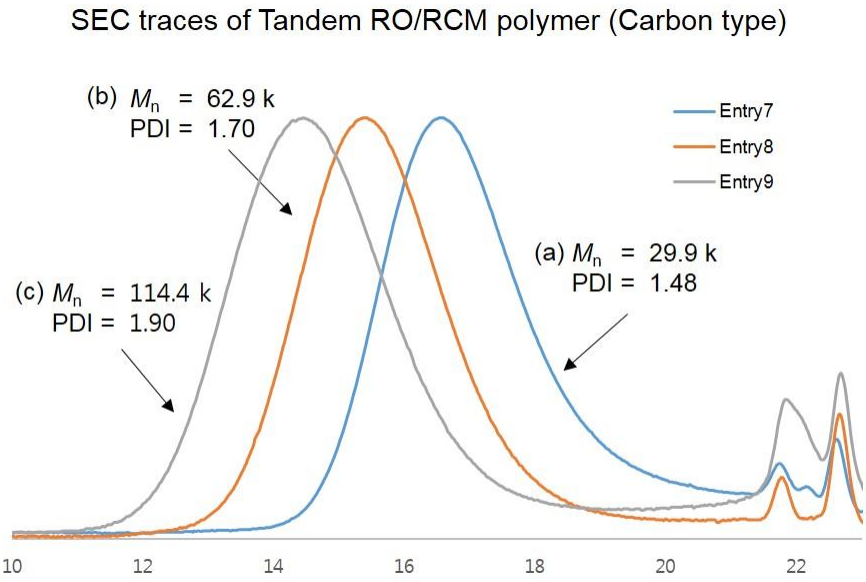


Figure S7. THF SEC trace for the tandem RO/RCM carbon type polymer. Molecular weights and PDIs are listed in the figure. (a) SEC trace of Table1-Entry7. (b) SEC trace of Table1-Entry8. (c) SEC trace of Table1-Entry9.

^{1}H-NMR & ^{13}C-NMR of tandem RO/RCM polymer & MOMP polymer

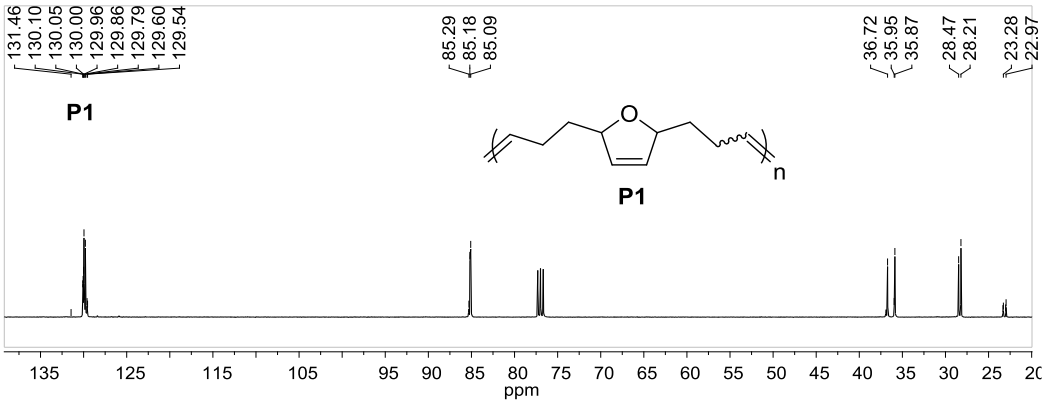


Figure S8. ^{13}C NMR of ether type tandem RO/RCM polymer

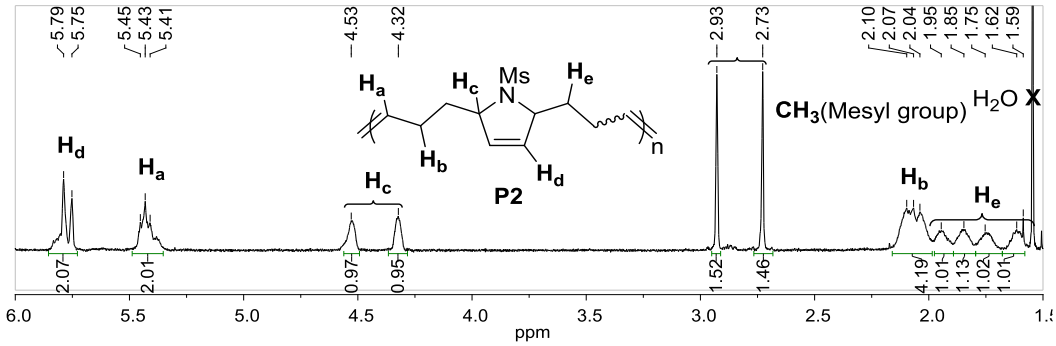


Figure S9-1. ^{1}H NMR of amide type tandem RO/RCM polymer

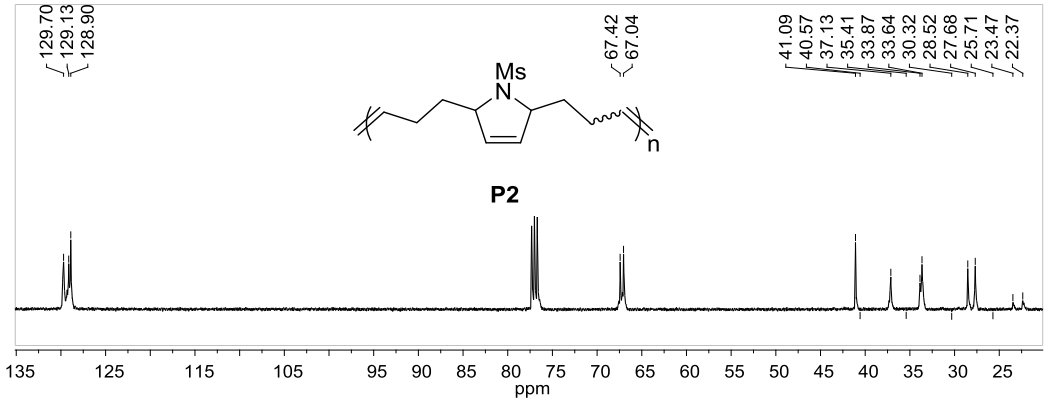


Figure S9-2. ^{13}C NMR of amide type tandem RO/RCM polymer

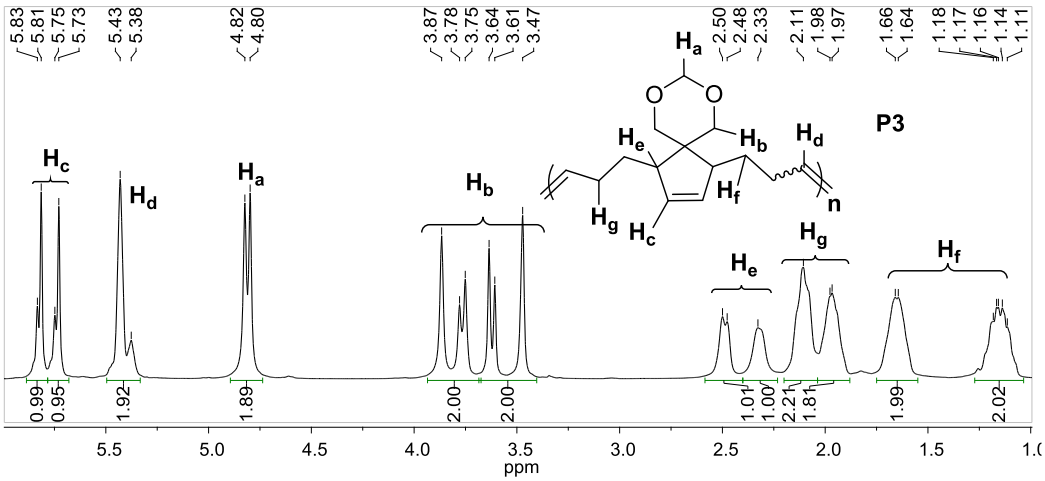


Figure S10-1. [1]H NMR of carbon type tandem RO/RCM polymer

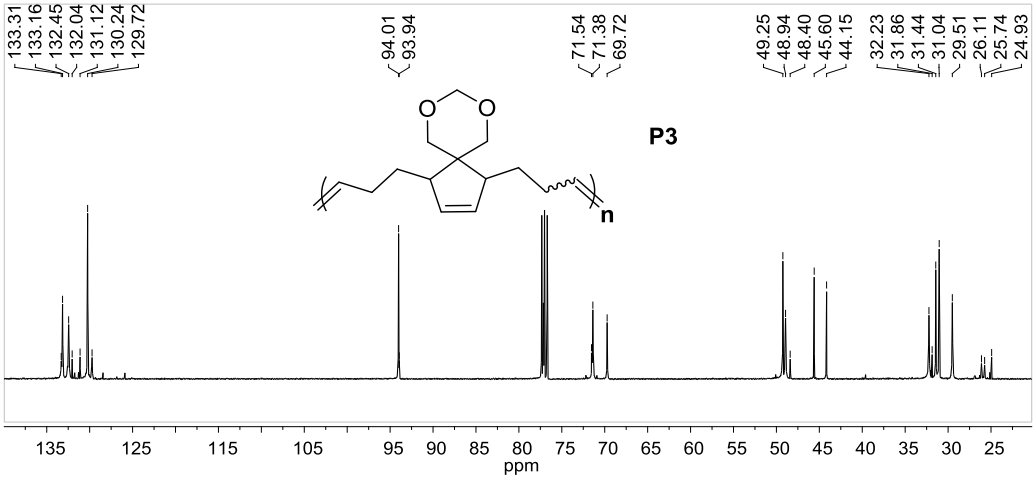


Figure S10-2. [13]C NMR of carbon type tandem RO/RCM polymer

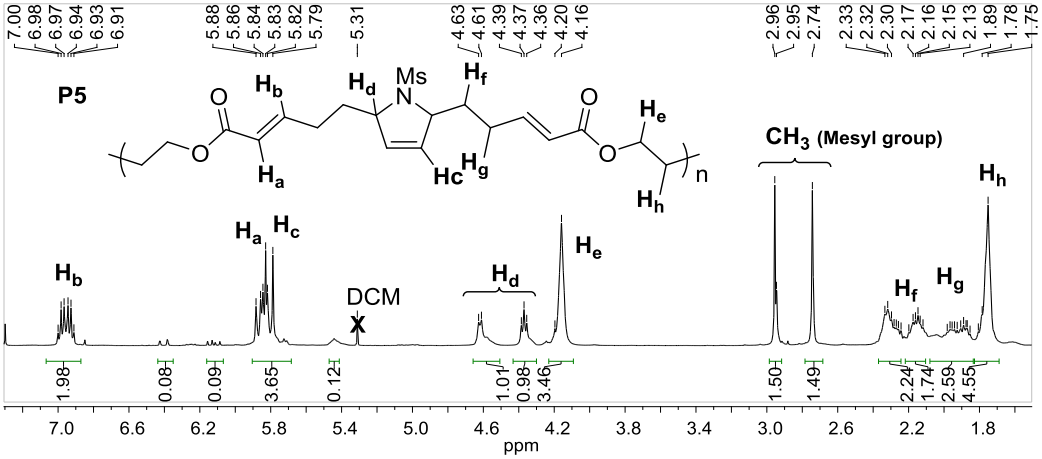


Figure S11-1. [1]H NMR of Mesyl amide type multiple olefin metathesis polymer

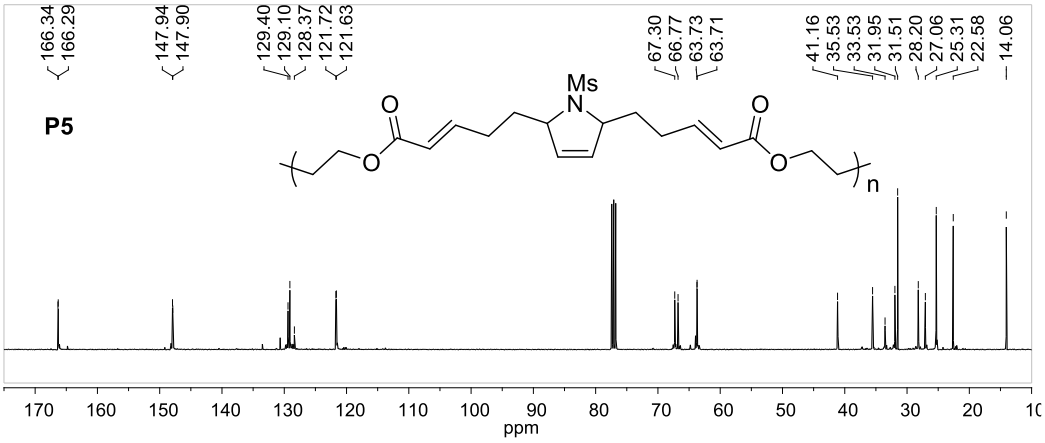


Figure S11-2. ^{13}C NMR of Mesyl amide type multiple olefin metathesis polymer

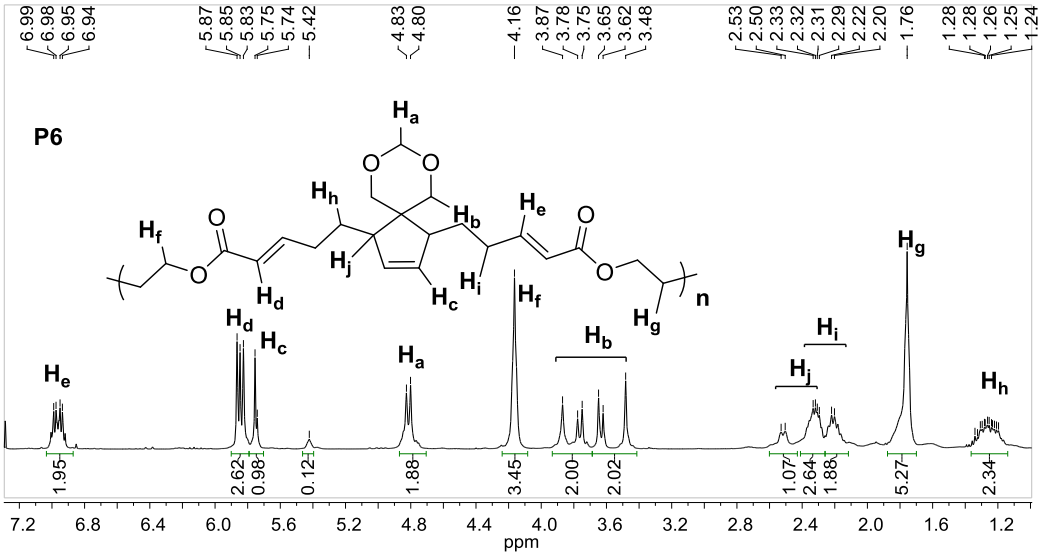


Figure S12-1. ^{1}H NMR of carbon type multiple olefin metathesis polymer

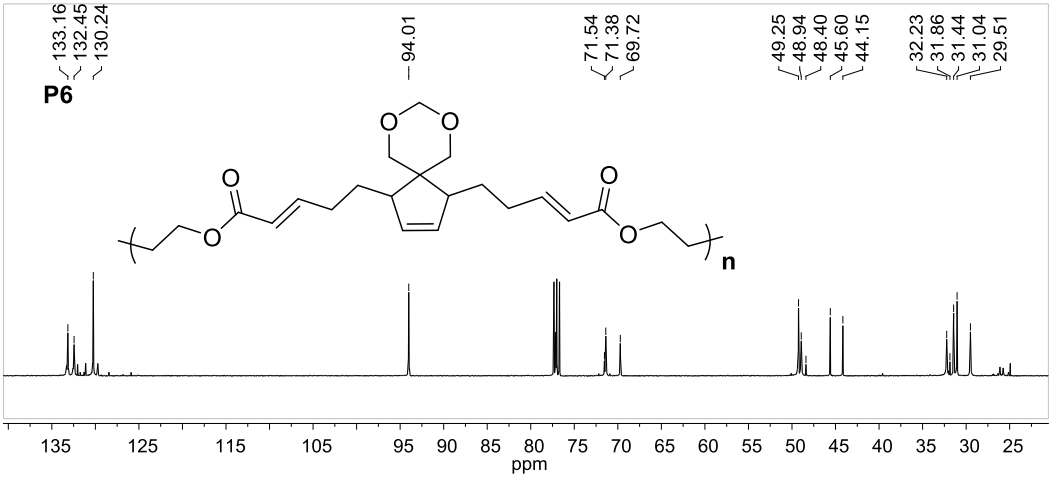


Figure S12-2. ^{13}C NMR of carbon type multiple olefin metathesis polymer

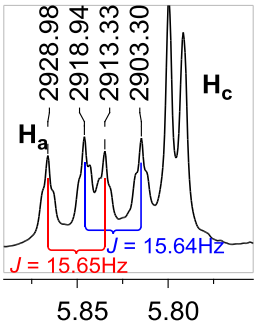


Figure S13-1. ^{1}H NMR of **P4** of magnified H_a signal with its coupling constants.

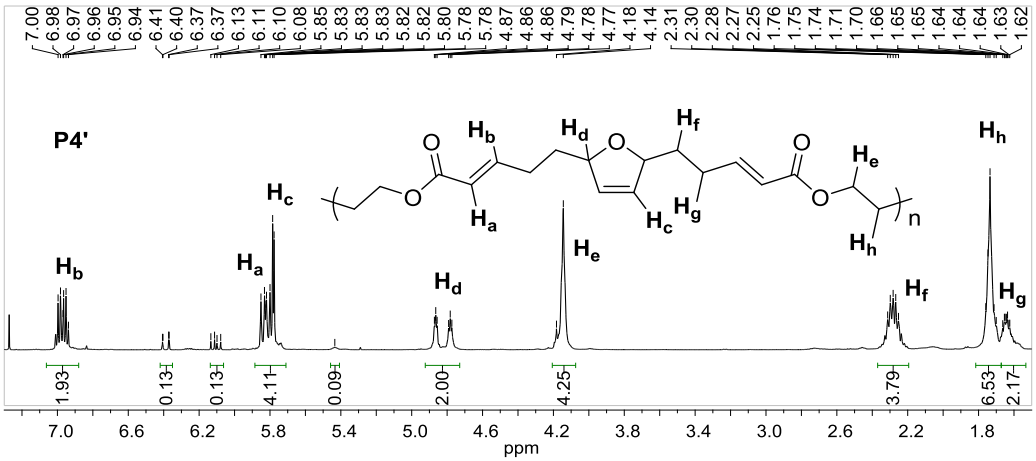


Figure S13-2. ^{1}H NMR of ether type multiple olefin metathesis polymer (one-pot method)

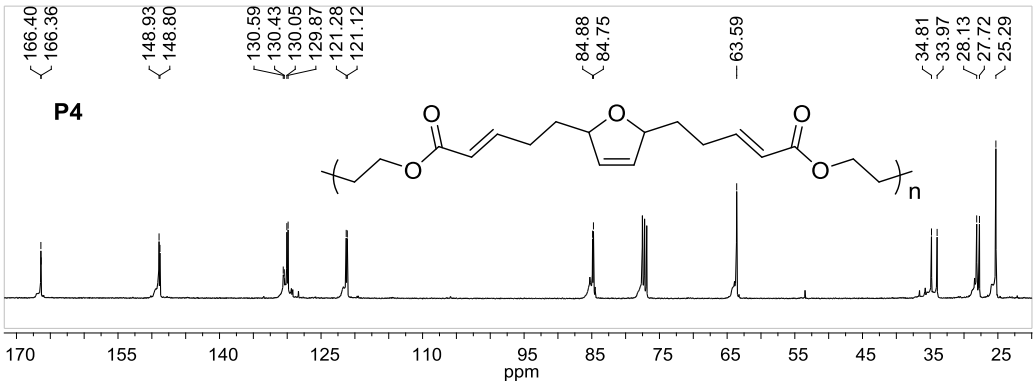


Figure S13-3. ^{13}C NMR of ether type multiple olefin metathesis polymer

^{1}H-NMR & ^{13}C-NMR of monomer

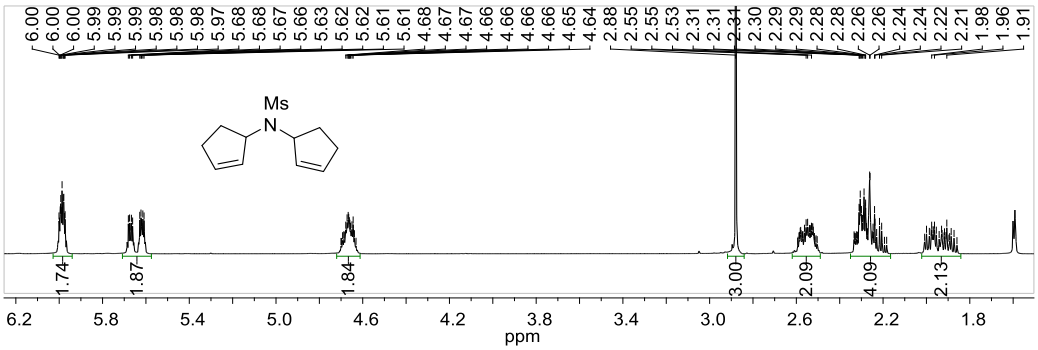


Figure S14-1 ^{1}H-NMR of **M2**

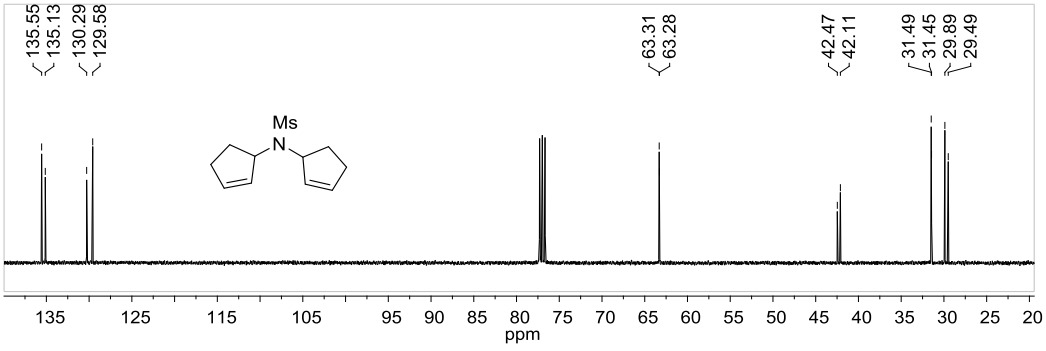


Figure S14-2 ^{13}C-NMR of **M2**

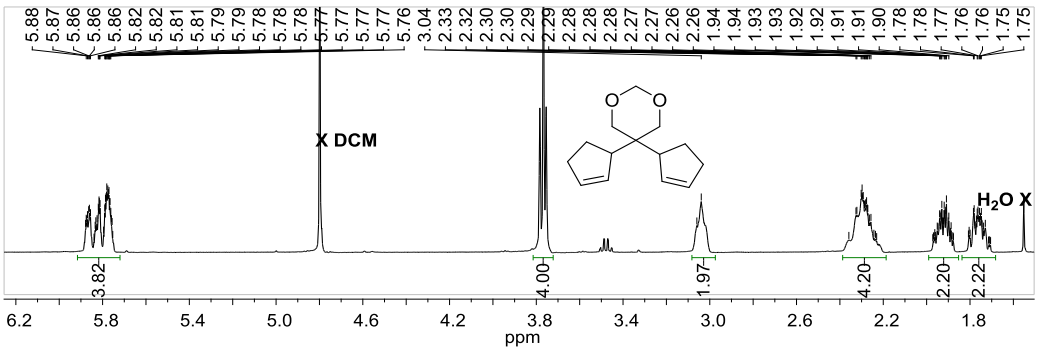


Figure S15-1 ^{1}H-NMR of **M3**

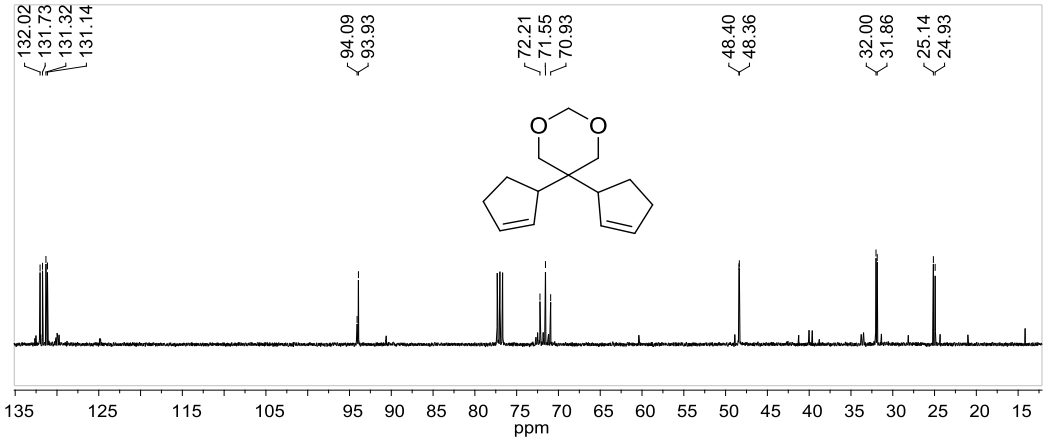


Figure S15-2 ^{13}C-NMR of **M3**

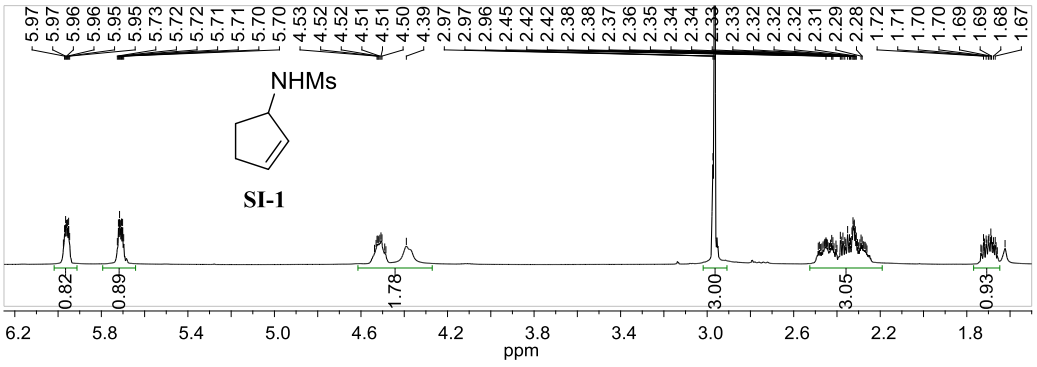


Figure S16-1 ^{1}H-NMR of **SI-1**

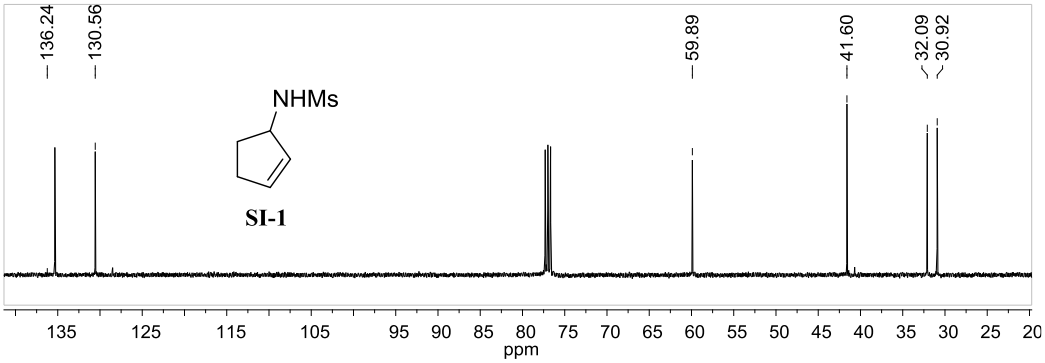


Figure S16-2 ^{13}C-NMR of **SI-1**

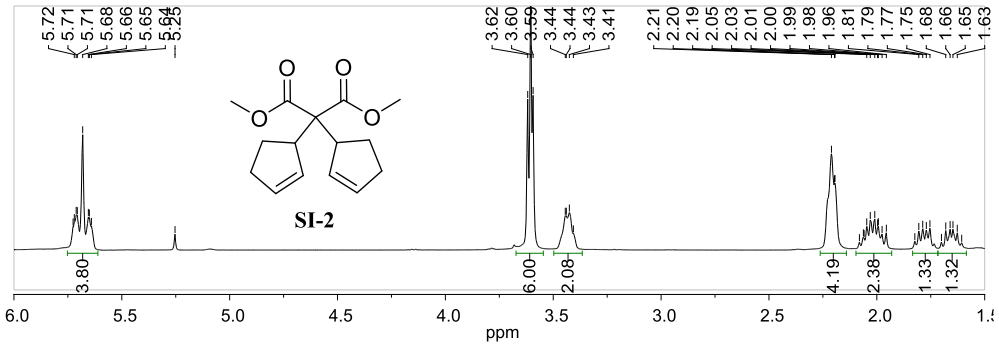


Figure S17-1 ^{1}H-NMR of **SI-2**

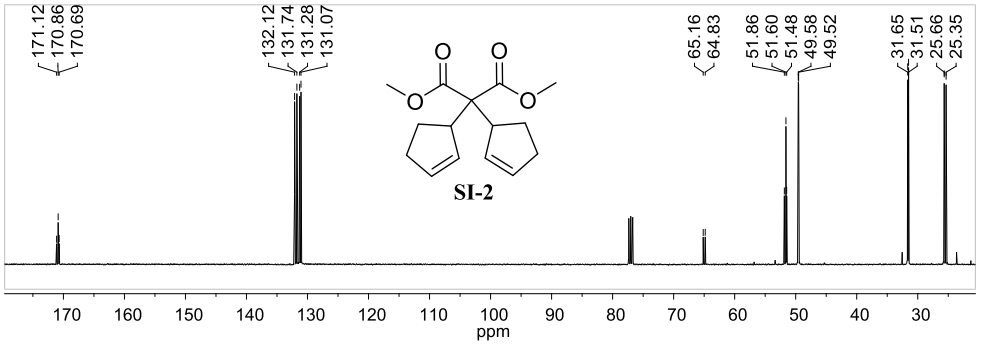


Figure S17-2 ^{13}C-NMR of **SI-2**

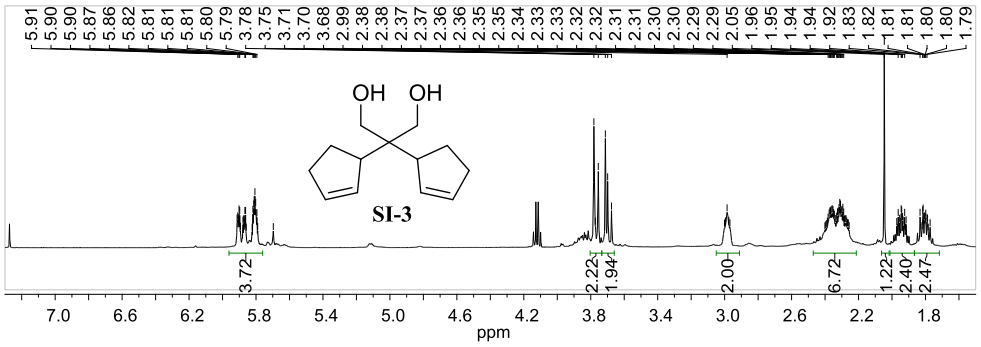


Figure S18-1 ^{1}H-NMR of **SI-3**

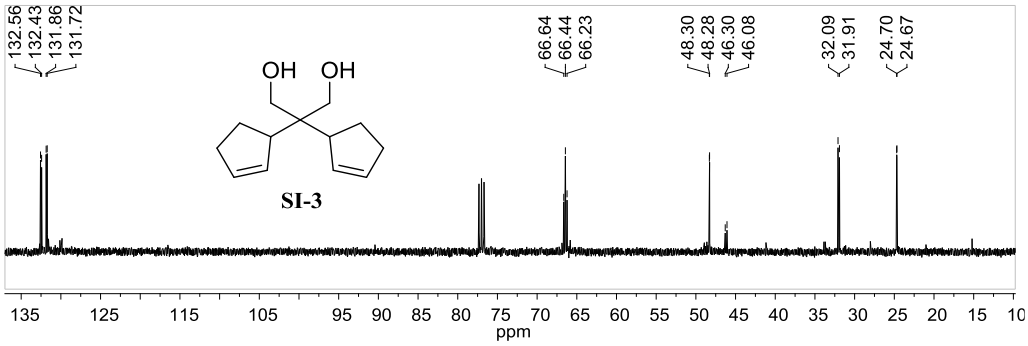


Figure S18-2 ^{13}C-NMR of **SI-3**

Diastereomeric repeat unit analysis by Ethenolysis

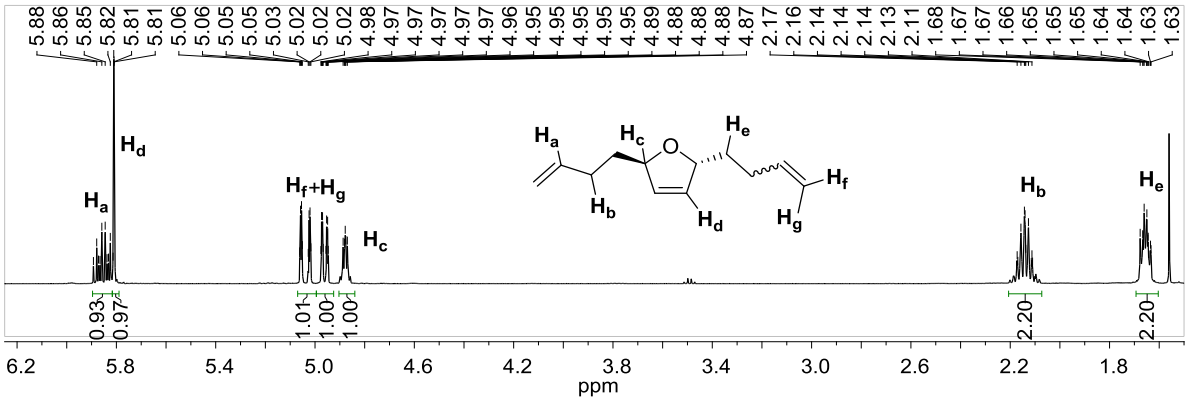


Figure S19-1 ^{1}H-NMR of **Ether type small molecule (*anti-form*)**

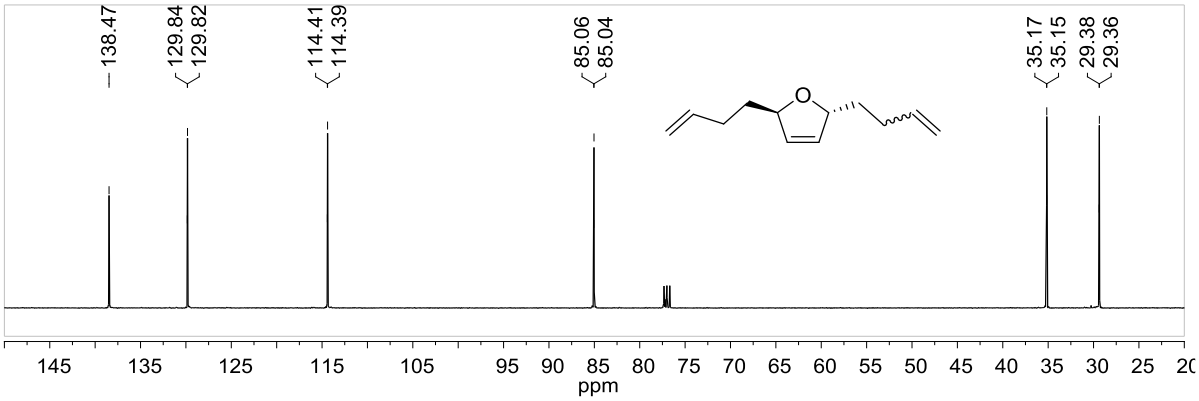


Figure S19-2 ^{13}C-NMR of **Ether type small molecule (*anti-form*)**

HRMS (CI+) calcd.for $C_{12}H_{19}O^{+}$ 179.1436 found, 179.1436

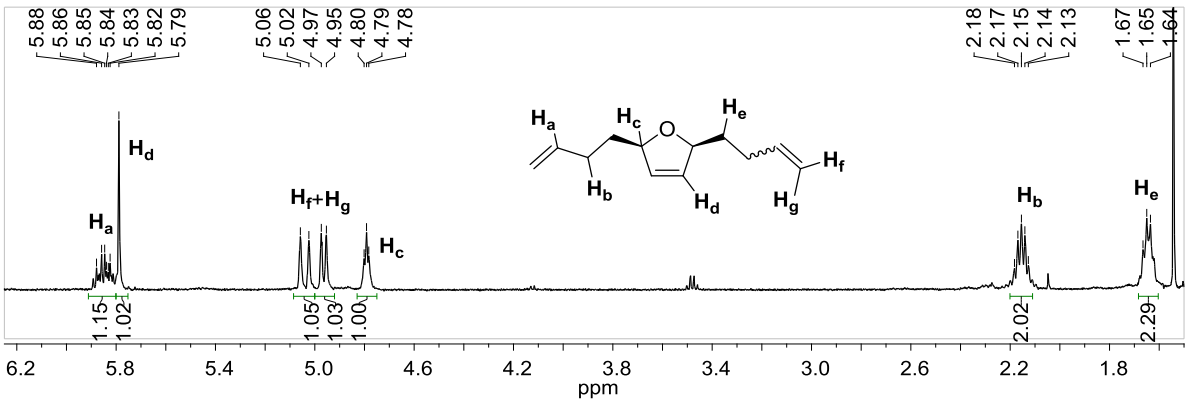


Figure S20-1 ^{1}H-NMR of **Ether type small molecule (*syn-form*)**

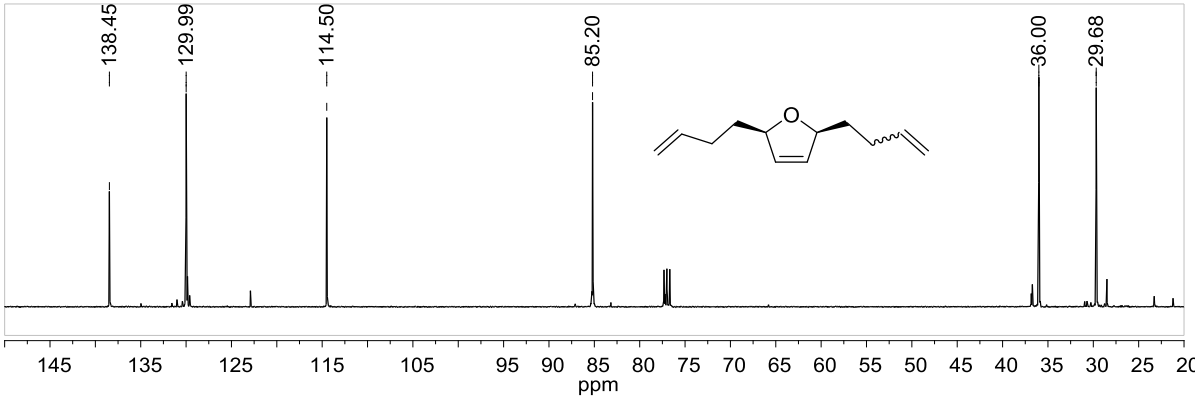


Figure S20-2 ^{13}C-NMR of **Ether type small molecule (*syn-form*)**

HRMS (CI+) calcd.for $C_{12}H_{19}O^+$ 179.1436 found, 179.1436

Ref : Brichacek. M; Batory. L.A.; Njardarson. J. *Angew. Chem. Int. Ed*. **2010**, *49*, 1648

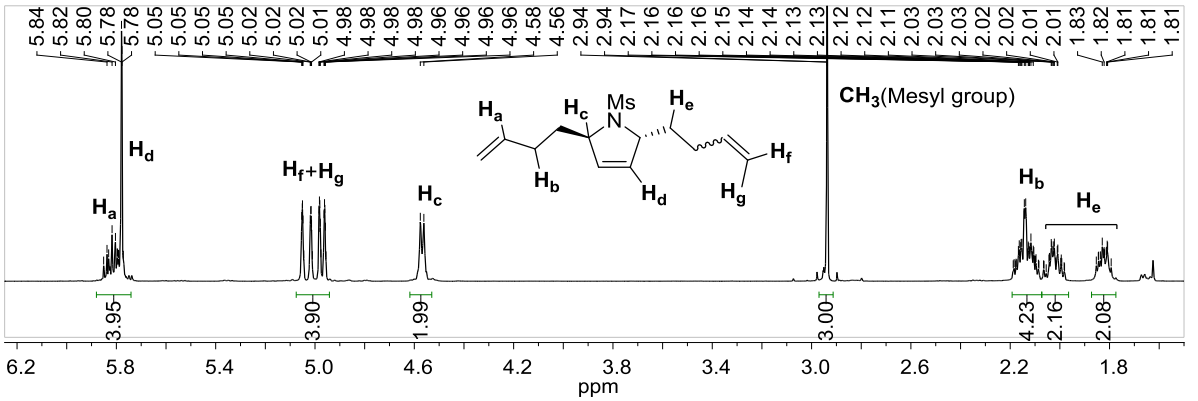


Figure S21-1 ^{1}H-NMR of **Mesyl type small molecule (*anti-form*)**

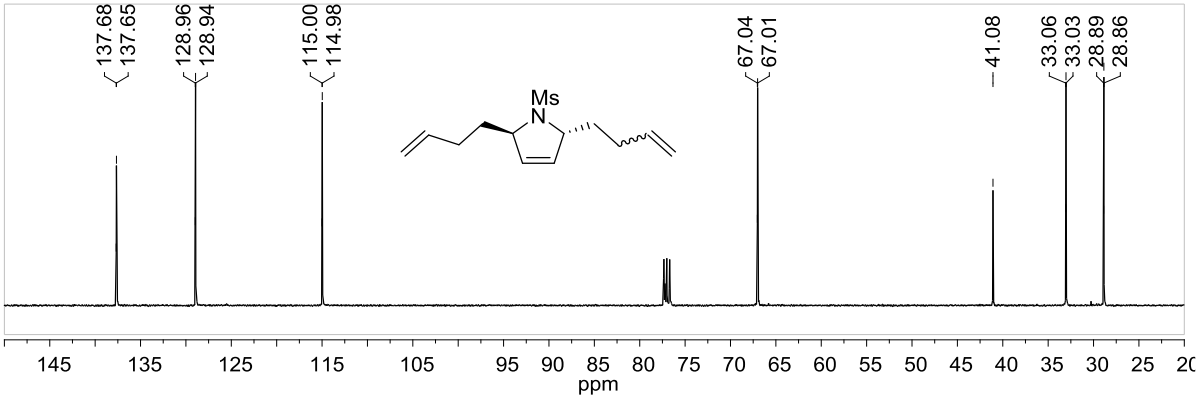


Figure S21-2 ^{13}C-NMR of **Mesyl type small molecule (*anti-form*)**

HRMS (CI+) calcd.for $C_{13}H_{22}NO_2S^+$ 256.1371 found, 256.1371

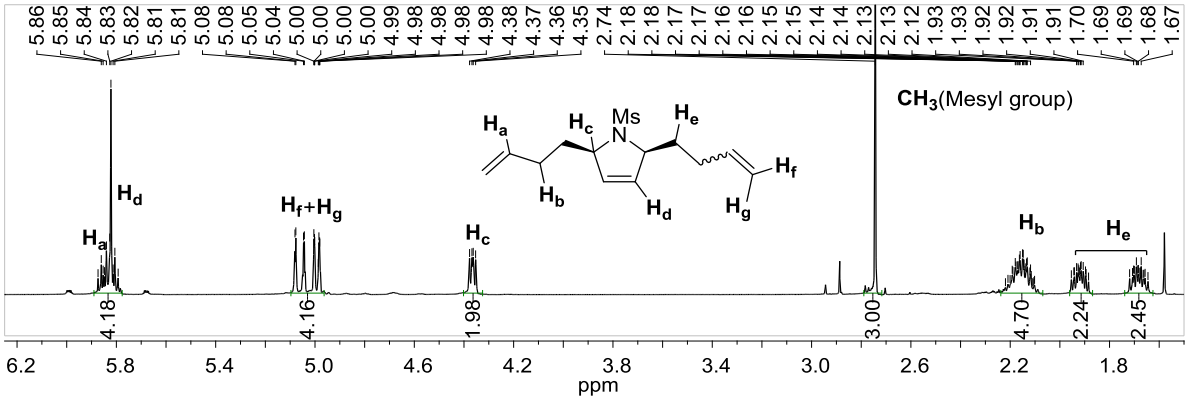


Figure S22-1 ^{1}H-NMR of **Mesyl type small molecule (*syn-form*)**

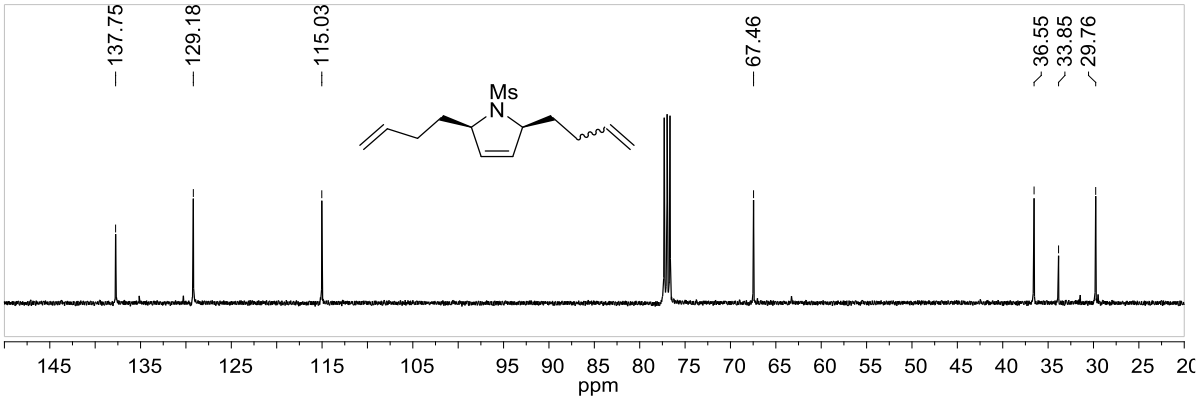


Figure S22-2 ^{13}C-NMR of **Mesyl type small molecule (*syn-form*)**

HRMS (CI+) calcd.for $C_{13}H_{22}NO_2S^+$ 256.1371 found, 256.1371

Ref: Ohno, H.; Kadoh, Y.; Fujii, N.; Tanaka, T. *Org. Lett.* **2006**, *8*, 947

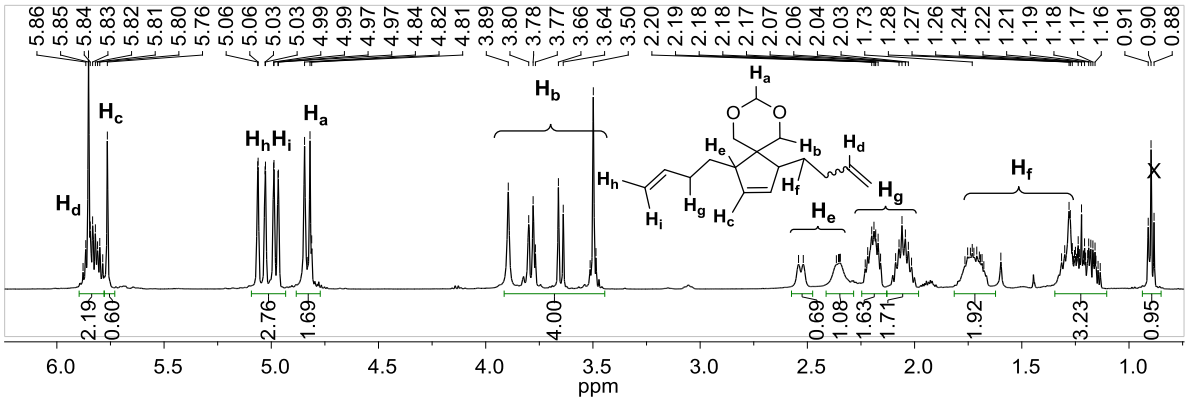


Figure S23-1 ^{1}H-NMR of **carbon type small molecule (*racemic form*)**

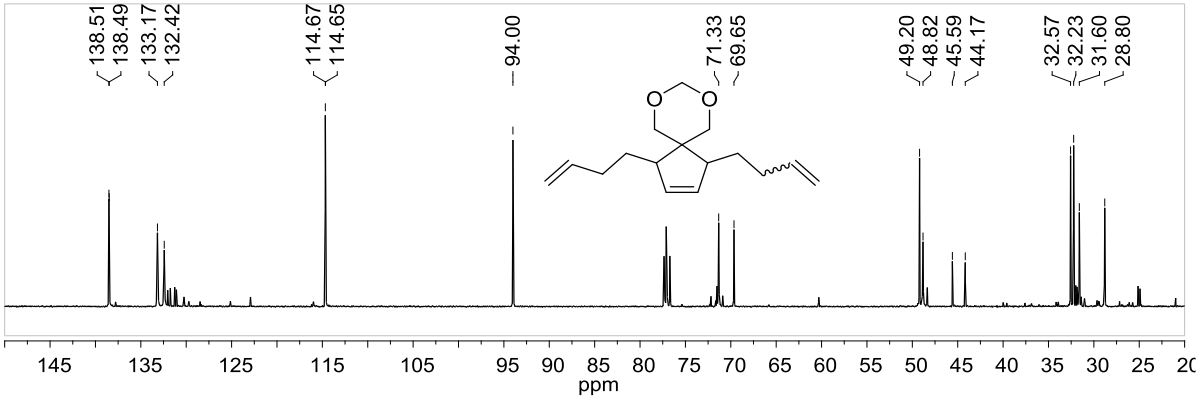


Figure S23-2 ^{13}C-NMR of **carbon type small molecule (*racemic form*)**

HRMS (CI+) calcd.for $C_{16}H_{25}O_2^+$ 249.1855 found, 249.1855